Molar Entropies — Let's understand some.

		$S\ (J\,K^{-1}\,mol^{-1})$	
$H_2O\ (s)$	smaller ↓	41.0	solid most ordered
$H_2O\ (l)$		63.2	liquid less, but still small V
$H_2O\ (g)$	larger ↓	188.3	large V, lots of ways to arrange

liquid more like a solid than a gas.

System vs. Surroundings

Place an ice cube tray with water in a ~~refrigerator~~ freezer

Water (l) → water (s)

$\Delta S_{water} < 0$ Decrease in entropy. Whoops!

But the refrig/freezer pumped heat out into the surrounding air, increasing its entropy

$$\Delta S_{water} + \Delta S_{surroundings} > 0$$

	$S\ (J\,K^{-1}\,mol^{-1})$
Very ordered → Carbon (diamond)	2.4
Less ordered Carbon (graphite)	5.7

Soft. Smudge (Internal sliding)

ΔS for reactions

Gases are easy.

Entropy is a bulk phenomenon

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$

3 molecules reduces to 2 molecules (really moles of)

Entropy increase or decrease?

Fewer ways to arrange 2 molecules → Decrease

$\Delta S^\circ = -88.9\ J\,K^{-1}\,mol^{-1}$

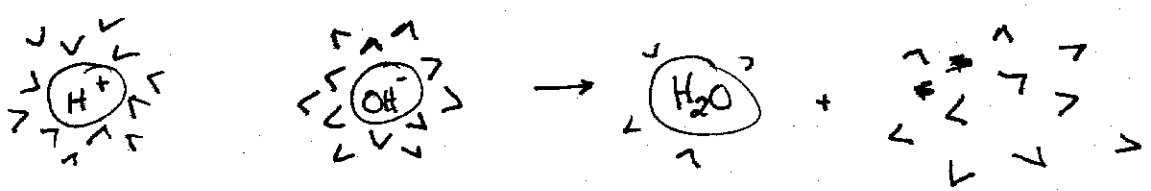
Liquids harder

(2) $NH_4^+(aq) + CO_3^{2-}(aq) \rightarrow NH_3(aq) + HCO_3^-(aq)$ $\Delta S = +146\ J\,K^{-1}\,mol^{-1}$

- NH_4^+: highly solvated
- CO_3^{2-}: Very highly solvated
- NH_3: moderately solvated (not charged)
- HCO_3^-: highly solvated

Two goes to One – Decrease? No!

(1) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\Delta S = +81\ J\,K^{-1}\,mol^{-1}$



lot of ordered water allowed to become disordered

$S = k \ln N$ ← Molecular interpretation

N = # ways of arranging (# of microscopic states)

Calculating entropy → $\Delta S = \frac{q_{REV}}{T}$

Measure reversible heat transfer at constant temperature

ice (0°C) ⟶ water (0°C). (and 1 atm)

Can calculate q_{REV} from enthalpy of melting
Temperature is constant, so $\Delta S = \frac{q_{REV}}{T}$ is easy.

If temperature changes during a process/reaction, then we could calculate small $q_{REV,i}$ for very small increments each at ~constant temperature, and add them

Better yet! → Integrate

FOR ① ⟶ ②

$$\Delta S = \int_1^2 dS = \int_1^2 \frac{dq_{REV}}{T}$$ (T varying along the integral)

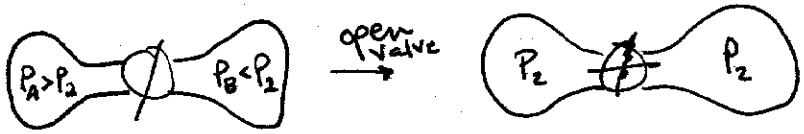
Can only calculate for the reversible path, but result will be true of any ① → ②

WHY? → S is a state variable

Stochastic vs. Bulk

Remember that S (and other thermo parameters) are statistical in origin

Therefore one cannot talk about S for 1 molecule. It is a bulk property.

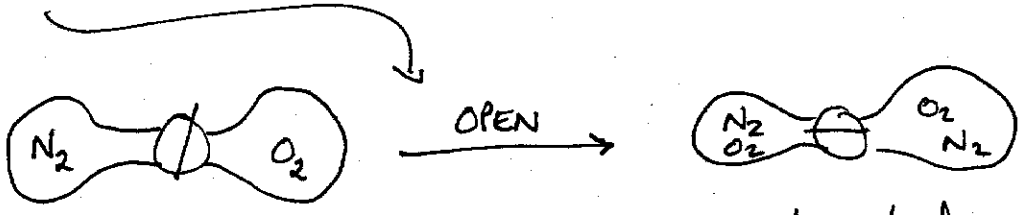


Gas overall will flow left to right.

Entropy drive → more ways to arrange when the pressure is uniform

(Convince yourself!)

WHAT HAPPENS?



entropy higher (entropy of mixing)

In both cases, entropy of system increases.

Both can take place without changing entropy of surroundings

$$\Delta S_{sys} + \Delta S_{surr} > 0$$

Expansion/mixing occurs spontaneously – does not require interaction with surroundings. ΔS_{surr} could be 0

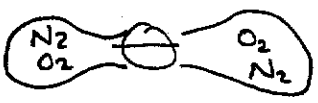
The reverse will not happen spontaneously. Would require interaction with surroundings.

What would $\Delta S_{surroundings}$ HAVE TO BE?

$<, \sim, > 0$

$\Delta S_{sys} < 0$ therefore $\Delta S_{surroundings}$ MUST BE greater than 0

Once we reach:



individual O_2's may go left or right (will), but on average, #'s will be ~equal.

BULK EFFECT

Chemical Reactions

$$H_2O\ (l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g)$$

What is ΔS°?

$$\Delta S^\circ = \bar{S}^\circ_{H_2(g)} + \tfrac{1}{2}\bar{S}^\circ_{O_2(g)} - \bar{S}^\circ_{H_2O(l)}$$

$$130.68 + \tfrac{1}{2}(205.14) - 69.91 \text{ J K}^{-1}\text{mol}^{-1}$$

$$= 163 \text{ J K}^{-1}\text{mol}^{-1}$$

THIRD LAW

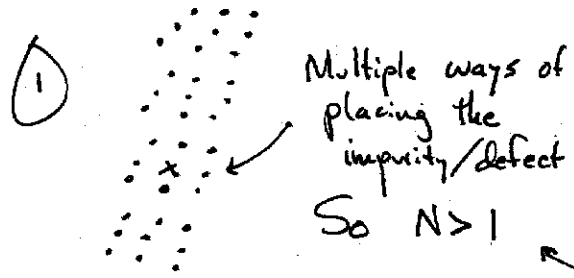
$$S_A(T = 0\,K) = 0$$

Why?

For a pure perfect crystal there is only one way to arrange. At 0K there is no motion (bringing disorder)

So, if $N = 1$, then $S = 0$

Why "pure," "perfect"?



Another way of saying this

If we had (1) and $S = 0$

We could remove x to create

Now perfectly ordered →

lower entropy (can't be $S < 0$)

$\leq$ not ΔS

Calculating Entropy

constant

$$dq_{REV} = C\,dT$$

Heating / Cooling →

We know $S_2 - S_1 = \int \frac{dq_{REV}}{T} = \int_{T_1}^{T_2} C\frac{dT}{T}$

At constant P,

$$S_2 - S_1 = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln T_2/T_1$$

Similarly

At constant V, $S_2 - S_1 = C_V \ln T_2/T_1$

So, as we saw before, if we want ΔS for a reaction at $T \neq 298$, we can break into paths